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SATURATED HYDROCARBON POLYMERIC BINDER

FOR ADVANCED SOLID PROPELLANT



PERIOD COVERED: January 1, 1969
to
March 31, 1969

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100.

Report Edited By: James E. Potts

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Publication Date: July 1, 1969

Jet Propulsion Laboratory Contract No. 951210

Technically Managed By: H. E. Marsh, Jr. - JPL

UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS
Polymer Research and Development
Bound Brook, New Jersey

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TECHNICAL CONTENT STATEMENT

This report contains information prepared by Union Carbide Corporation, Chemicals and Plastics Operations Division, under J.P.L. subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology or the National Aeronautics and Space Administration.

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I. OBJECTIVE

Union Carbide Corporation, Chemicals and Plastics Operations Division has agreed to assist the Jet Propulsion Laboratory, California Institute of Technology, on a level of effort basis, in the development of a new or improved polymeric binder for advanced solid propellant and hybrid propellant grains. The general objectives are described in Quarterly Report No. 1.

II. ABSTRACT

Two different end group conversion procedures were applied to produce carboxyl terminated prepolymers from ω -bromoester telomers of ethylene with propylene.

In one of the methods, based upon nucleophilic displacement of terminal bromide by the anion of methyl thioglycolate, some measure of success has been obtained, however, the conversion of bromide terminal groups was not quantitative.

The other method using displacement of terminal bromide with cyanide ion followed by hydrolysis to carboxyl has thus far given negative results.

Terpolymers of ethylene, propylene and butadiene have been prepared which are difunctional in terminal ester groups. Hydride reduction followed by hydrogenation has given saturated liquid diols from one of these products. A direct correlation between butadiene content and ester functionality was established.

The thin layer chromatographic methods applied previously in our program have been used to analyze prepolymers with different backbones and functional groups. The method was found to be of general utility for the qualitative analysis of prepolymers functionality distribution.

III. SCOPE.

The scope of our program remains as previously outlined.

IV. INTRODUCTION

In previous quarterly reports as well as in our triennial report, we have discussed the preparation of telomers of ethylene with α -olefins other than neohexene. The most promising results were obtained with propylene. In the report to follow we present the results of some reaction studies on converting the end groups in ethylene/propylene telomers into useful functional groups.

We also will report some interesting results obtained when butadiene is added to an ethylene/propylene copolymerization mixture.

The results of our examination of the general utility of thin layer chromatography for the characterization of other prepolymers systems than our own carboxyl terminated prepolymers will also be discussed.

V. TECHNICAL DISCUSSION

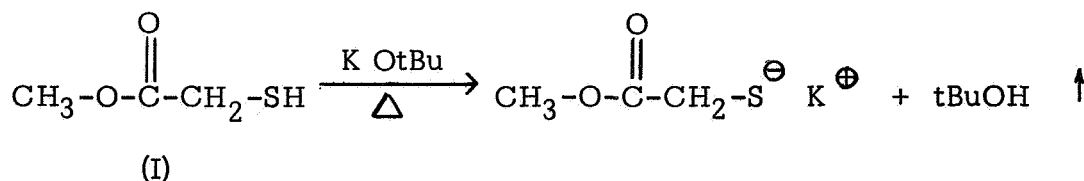
A. Ethylene/Propylene Telomers - Chemical Modification of Terminal Groups

We have previously reported that attempts to convert the terminal bromide of the ethylene/propylene telomers to a carboxyl group failed when we used the methods which were successful for the ethylene/neohexene telomers. The reason we proposed for this was that the less sterically hindered terminal bromides in the ethylene/propylene telomers were more subject to displacement than those in the ethylene/neohexene telomers. This resulted in a large amount of terminal OH or acetate when KOH or KOAc were used, respectively, for melt dehydrobromination reactions. Since terminal unsaturation was essential for the subsequent ozonolysis and oxidation steps, the final COOH functionality was less than calculated based on the starting material's ester and bromide functionality.

It was proposed at that time that several reactions based upon displacement of terminal bromide might be feasible and lead to higher carboxyl functionalities:

1. Displacement of Br^\ominus by thioglycolate ion.
2. Sulfide coupling of two molecules resulting in displacement of two Br^\ominus .
3. CN^\ominus displacement of Br^\ominus followed by hydrolysis.

Reaction (1) was tried on 22 grams of ethylene/propylene telomer 27-EMS-40 (Mol. Wt. = 819, 0.81 Br per molecule). An equimolar quantity of potassium *t*-butoxide and a twofold molar excess of methylthioglycolate (I) was added to the polymer dissolved in 50 ml. dry diglyme solvent.



When the reaction mixture was heated at 150°C, 1.6 g. of a distillate (probably *t*-butanol) was obtained, bp 75-90°C, and a white solid (later shown to be KBr) precipitated. An aliquot of the organic layer was worked up and the recovered product analyzed. A positive (but very weak) Beilstein test for halogen was obtained and the infrared spectrum showed an increase in the ester absorption, but no significant changes in the C=C region.

The reaction mixture was then refluxed with an excess of aqueous KOH to saponify all ester end groups and the methyl thioglycolate. After acidification and workup as usual, 20 grams of product were obtained. Mol. Wt. = 960, neutralization equivalent = 1230. T.L.C. shows a large non-functional fraction. However, the infrared spectrum shows ester absorption as well as COOH absorption, which indicates that the saponification step did not proceed to completion.

The product from the above experiment was then further treated by melt saponification using an excess of finely divided KOH at 150°C for 20 minutes. The product was recovered by acidification with acetic acid, taking up the polymer in heptane and water washing prior to drying and vacuum stripping to give the liquid product, neutralization equivalent = 1052.

The infrared spectrum showed an increase in the carboxyl content of about twofold, with no ester remaining at all.

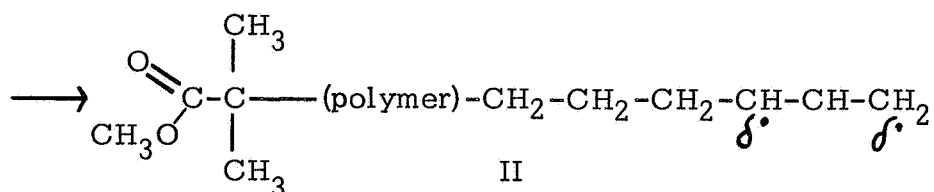
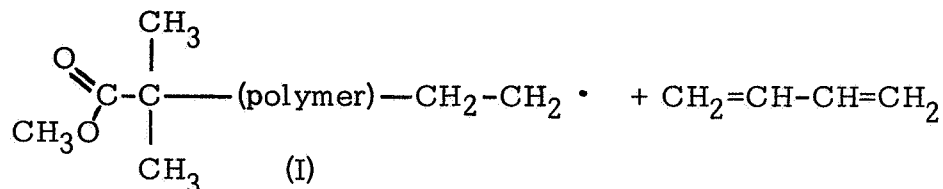
Thin layer chromatography (in 2% methanol in CHCl₃) showed a decrease in the nonfunctional fraction as compared with the starting material as well as an increase in both the mono- and difunctional components, presumably due to saponification of the ester groups which behave like nonfunctional ends in this T.L.C. system.

As yet we have not attempted to utilize reaction (2) proposed above.

To test reaction (3) 20 grams of another ethylene/propylene sample 27-EMS-34-1 (Mol. Wt. = 1050, .72 Br per molecule) was treated with a large excess of KCN in DMSO solvent. The reaction mixture was heated briefly to 100°C with stirring under nitrogen and then kept at 60°C overnight. The product was taken up in heptane and washed with water to remove excess KCN and the DMSO. After evaporation, 18 grams of product were obtained having a strong positive Beilstein Test and showing weak CN absorption in the infrared, corresponding to about .11 CN per molecule or about 14% reaction. A possible reason for the failure of this reaction to go to completion may lie in the inhomogenous nature of the reaction mixture: The telomer is nearly insoluble in the KCN/DMSO layer.

B. Ethylene/Propylene Butadiene Terpolymers

Incorporation of a small quantity of butadiene into an ethylene/propylene copolymerization offered the possibility that rather stable polymer radicals would result when butadiene reacted with a growing ethylene/propylene copolymer chain I:



The resonance stabilized radical II could then persist long enough to become terminated by recombination with other radical species (such as another radical like itself or a radical derived from the initiator). The experiment described below was performed to see if this terpolymerization approach would lead to interesting prepolymers.

Run 27-EMS-132 was performed in the Unit II continuous stirred autoclave reactor. The charge to the reactor contained 42.49% ethylene, 41.20% propylene, 4.30% butadiene and 2.00% DMAB and 10% benzene. After steady state had been reached the reactor was operated at 106-109°C, 35,000 psi and at a feed rate of 4710 gms./hr. In 35 minutes of steady state operation 30 gms. of copolymer was obtained -- a tan colored oil of 180 cps viscosity at 21°C.

Infrared spectroscopy showed the presence of both vinyl and trans-disubstituted double bonds as well as the ester end groups derived from DMAB.

Vapor phase osmometry in benzene solution gave a value of 550 for the number average molecular weight. Combining this result with the elemental oxygen content of 12.91 wt. %, we calculate an O₂ functionality of 2.2.

We have also examined the above product by nuclear magnetic resonance (N.M.R.) spectroscopy and have found that in spite of the low butadiene content in the feed to the reactor, the product (obtained at a fairly low conversion) contained a significantly high proportion of butadiene. The analysis indicated 42 wt. % butadiene, 7 wt. % propylene, 12 wt. % ethylene and 39 wt. % end groups derived from the DMAB initiator. From these values we obtain an equivalent weight of 260 based on the ester

functionality present. When combined with the VPO number average molecular weight of 550, this gives an average functionality of 2.1 ester groups per molecule, in reasonable agreement with the value determined by the oxygen elemental analysis and reported above.

When 20 grams of this terpolymer was reduced with lithium aluminum hydride in ether, 17 grams of liquid product resulted which exhibited only a trace of ester carbonyl absorption in the infrared, but a very intense hydroxyl band at 3400 cm^{-1} . The unsaturation still remained at this point.

Hydrogenation of 16 grams of the hydroxyl terminated product using Raney nickel catalyst gave 13 grams of a yellow oil which showed none of the original unsaturation bands in the infrared. Hydroxyl content was determined by the phthalic anhydride/pyridine method and found to be 4.12 meq/g, corresponding to an equivalent wt. of 243. The V.P.O. molecular weight was 546 indicating an overall hydroxyl functionality of 2.2 per molecule.

Since the 1,4 polymerized butadiene residues give two ethylene units upon hydrogenation and the 1,2 polymerized residues yield butene-1 units, the final product is essentially a difunctional hydroxy terminated liquid ethylene/propylene copolymer containing ethyl branches derived from the original 1,2-polymerized butadiene residues.

Several variations in this basic copolymer synthesis are possible which may lead to useful rocket binder materials:

1. The method as actually completed involving hydride reduction/hydrogenation leading to saturated liquid diols.
2. Hydrolysis of the initial product followed by hydrogenation leading to saturated liquid diacids.
3. Hydrolysis or hydride reduction followed by addition of the vinyl groups leading to trifunctional binder components.
4. Use of AIBN as the initiator followed by hydride reduction/hydrogenation leading to saturated liquid diamines.

To further explore the scope of this terpolymerization we made additional runs at different butadiene contents. In these runs our goal was to prepare terpolymers of lower butadiene content, and still retain the desirable difunctionality apparently conferred by butadiene to the product.

The terpolymerizations were run in the continuous stirred autoclave reactor at 110-114°C with pressures up to 35,000 psi. The butadiene content in the reactor charge was varied between 0.25 and 4.35 wt. % in the different runs of this series. 1.00 wt. % DMAB initiator was used in each of the runs. The results of these runs are shown in the table below:

Run #28-EMS-	27	44	45	66	67
Wt. % Butadiene in Charge	4.35	2.23	1.13	0.50	0.25
% Conversion	2.00	1.92	2.24	4.21	7.53
Wt. % Butadiene in Product	48.3	39.0	30.2	11.6	4.6
Molecular Weight	615	458	554	781	1022
Ester Functionality	1.88	1.57	1.46	1.58	1.18

The above data show that as the butadiene content of the terpolymer is reduced by decreasing the butadiene content in the charge, the functionality also decreases from nearly two ester groups per molecule to values below 1.5. The molecular weight of the product, as well as the yield, increase with decreasing butadiene content.

In the light of these findings we conclude that the incorporation of low levels of butadiene into a DMAB initiated ethylene/propylene copolymer does not allow the production of a difunctional terpolymer. Over 4 wt. % butadiene in the charge is needed in order for the functionality to approach 2; and in this range the butadiene incorporation into the terpolymers is near 50% by weight.

C. Application of Thin Layer Chromatography for the Analysis of Binder Prepolymers

We have applied our Thin Layer Chromatography (T.L.C.) methods for qualitative analysis of binder prepolymer functionality distribution to other prepolymers and binder ingredients. Some interesting and useful results were obtained. These were reported at the ICRPG meeting in Huntsville on March 12. The results presented demonstrated the following:

1. COOH terminated prepolymers can be characterized by T.L.C.

a. Use of a fairly polar eluting solvent such as 2% methanol in chloroform with silica gel plates results in separation of several types of COOH terminated prepolymers into well resolved components.

b. Correlation of the T.L.C. results with the known average functionalities of prepolymer fractions obtained by Column chromatography has allowed identification of the above components with the non-, mono- and difunctional prepolymer fractions. As expected the nonfunctional components are more easily eluted than the monofunctional components, which in turn are eluted more rapidly than the difunctional components.

c. Because of (a) and (b) a qualitative evaluation of prepolymer functionality distribution is possible in comparatively short times, 45 minutes to an hour in most cases.

d. The same T.L.C. method used for analysis of the COOH terminated prepolymers works well when applied to other binder ingredients such as Dimer and Trimer Acid.

2. OH terminated prepolymers can also be characterized by T.L.C.

a. Use of a less polar eluting solvent than described in 1-a is necessary for OH terminated prepolymers. 40% CHCl_3 in heptane has worked well for us and gives well resolved separations of such prepolymers as Telagen-S into three or more components.

b. Correlation of our T.L.C. results with column chromatographic studies by Muenker at ESSO allows identification of the above components as the non-, mono-, di- and possibly higher functional fractions of Telagen-S.

c. Having identified the components, a rapid qualitative evaluation of hydroxyl terminated prepolymer functionality distribution by T.L.C. is also possible.

3. Quantitative analyses of functionality distributions in prepolymers can also be accomplished by T.L.C. In our work a manually operated reflectance densitometer was used to obtain plots showing the variation of reflectance along the path of the eluted components on a T.L.C. plate. Resolved components show up as individual peaks on such a plot. The area under a given peak is proportional to the amount of that component present in the original mixture. For accurate work of this type, a determination of the proportionality constant between the "blackness" of the spot and the amount of the component present should be made for each component.

VI. PLANS FOR FUTURE WORK

In the quarter to come we plan to pursue an investigation of terpolymerization as a method for introducing reactive functional groups into prepolymers.

Emphasis will be placed upon terpolymers containing ethylene, propylene and a third monomer which will serve as a source of hydroxyl functionality.

A number of such systems will be evaluated to see if they lead to useful isocyanate curable prepolymers.

In an independent exploratory effort, Union Carbide has already prepared a series of such terpolymers based upon vinyl acetate, 3-hydroxy-3-methylbutene, and bicyclohept-5-ene-2-methylol as well as terpolymers containing carboxyl groups derived from acrylic acid and other functional groups.

We plan to evaluate some of the terpolymers produced in Union Carbide's exploratory program for use as solid propellant binder precursors as well as to synthesize a series of terpolymer samples specifically for binder application.